

Review

Metallophenanes bridged by group 13 elements



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Contents

1. Introduction and scope	115
2. Aluminum- and gallium-bridged [1]metallophenanes	116
2.1. The first generation: Trisyl-based ligands	116
2.2. Conclusions from the first generation	118
2.3. The second generation: The Mamx ligand	119
2.3.1. Metallopolymers	120
2.3.2. DFT calculations	120
2.4. Conclusions from the second generation	121
2.5. The third generation	122
3. Indium-bridged [1]metallophenanes	123
4. Boron-bridged [1]metallophenanes	125
4.1. Synthesis and mechanistic insights	125
4.2. Reactivity of bora[1]ferrophenanes	126
5. [n]Metallophenanes ($n \geq 2$)	128
6. [n.n]Metallophenanes	129
7. Conclusions	131
Acknowledgments	131
References	131

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ABSTRACT

Metallophenanes with one or multiple sandwich moieties and at least one group 13 element in bridging position are reviewed. The majority of this review summarizes publications concerned with strained sandwich compounds and their application as monomers for metal-containing polymers. Publications up to early 2015 are included.

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Abbreviations: Ar', 2-[(dimethylamino)methyl]phenyl; DSC, differential scanning calorimetry; DLS, dynamic light scattering; Fc, $\text{Fe}(\text{H}_4\text{C}_5)(\text{H}_5\text{C}_5)$; fc, $\text{Fe}(\text{H}_4\text{C}_5)_2$; FCP, ferrocenophane; GPC, gel permeation chromatography; Mamx, 2,4-di-*tert*-butyl-6-[(dimethylamino)methyl]phenyl; Me_2Ntsi , [(dimethylamino)dimethylsilyl]bis(trimethylsilyl)methyl; Mpysm, [dimethyl(2-pyridyl)silyl]methyl; PFS, poly(ferrocenylsilane); PS, polystyrene; Pytsi, [dimethyl(2-pyridyl)silyl]bis(trimethylsilyl)methyl; RCP, ruthenophane; ROP, ring-opening polymerization; trisyl, tris(trimethylsilyl)methyl.

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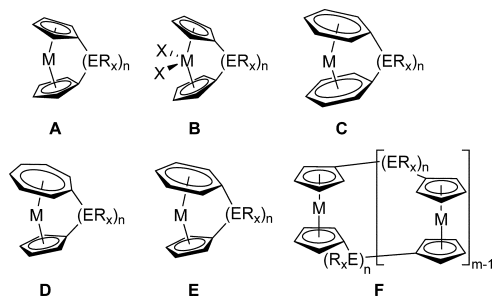


Fig. 1. Metallocyclophanes.

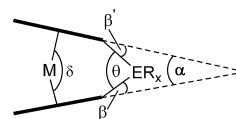
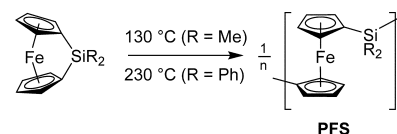


Fig. 2. Common angles to characterize distortions in [1]metallocyclophanes.



Scheme 1. Thermal ring-opening polymerization (ROP) of sila[1]ferrocenophanes [20].

1. Introduction and scope

[*n*]Metallocyclophanes are complexes where two metal-coordinated mancude-ring systems are linked by a bridging chain with *n* atoms in its backbone¹. This is illustrated in Fig. 1 for homoleptic (A–C) and heteroleptic compounds (D and E). The largest class is that of [*n*]metallocenophanes (A), with the most examples known for [*n*]ferrocenophanes (M=Fe). The family of species of type B could also be addressed as [*n*]metallocenophanes, but are more often called *ansa* complexes. If one considers the IUPAC definition [1] for metallocenes as sandwich complexes of the type bis(η^5 -cyclopentadienyl)metal, where the d metal is bonded *only* to the face of two cyclopentadienyl ligands, species of type B are not [*n*]metallocenophanes as the parent species are not metallocenes. However, in practice, this recommendation is not followed and species such as Cp₂MCl₂ are usually classified as metallocenes. More importantly, classes A and B are chemically very different. A short bridge in A forces the Cp rings to deviate from their coplanarity in the parent metallocenes Cp₂M, which is accompanied by a built-up of intrinsic strain. In contrast, the Cp rings in species B are naturally tilted as the metals in the parent compounds Cp₂MX₂ (M=Ti, Zr, Hf) are pseudo tetrahedrally coordinated. For B the *ansa* moiety restricts the flexibility of the structure and, commonly, these compounds are used for olefin polymerizations, in particular, in form of their chiral derivatives [2].

The best known class of the heteroleptic sandwich complexes is that of type D, which were coined trocicenophane (M=Ti), trovacenophane (M=V), and trochrocenophane (M=Cr) [3–5]. To date, examples of type E are only known for manganese and chromium [6–9]. In addition, other heteroleptic [*n*]metallocyclophanes are known, which are even rarer; e.g., the CH₂SiR₂-bridged cobalt complex [Co(η^4 -Me₃C₄-CH₂SiR₂- η^5 -C₅H₄)] equipped with a cyclobutadiene and a Cp moiety [10] and the (tBu₂Sn)₂ bridged titanium species [Ti{ η^5 -C₅H₄-(Sn_tBu₂)₂- η^8 -C₈H₇}] equipped with a cyclooctatetraene and a Cp ligand [11].

Metallocyclophanes can also exhibit more than one sandwich moiety. Such species are illustrated for metallocenophanes in structure F (Fig. 1), where *m* expresses the number of sandwich moieties and *n* is the number of bridging atoms. Using ferrocenophanes (FCPs) as an example, larger ring systems are commonly addressed as [*n*^{*m*}]ferrocenophanes, whereas for species with just a few

repeating units, the meaning of *m* is usually substituted by repeating *n*, such as in [*n.n*]FCPs (*m*=2) or [*n.n.n*]FCPs (*m*=3) [12].

Whereas in [*n*]metallocyclophanes with relatively short bridges the metal-coordinated rings are tilted relative to each other, rings coordinated to the same metal in [*n*^{*m*}]metallocyclophanes are coplanar and the structures of the sandwich moieties resembles those of the parent sandwich complex. However, the structures of [*n*]metallocyclophanes can be significantly different compared to the respective parent sandwich species. This is illustrated for [1]metallocyclophanes in Fig. 2, with the common set of angles that is used to measure the degree of distortion. The distortion or intrinsic strain of such a molecule translates into stored energy, a fact that makes these species potential candidates for polymerizations.

Shortly after the first [*n*]metallocyclophane was reported by Rinehart et al. in 1957 [A; M=Fe; (ER_x)_n=(CH₂)₂C(=O)] [13], the first strained sandwich compound, a [2]FCP with a C₂Me₄ bridge, was described by the same group [14]. The first strained sandwich compounds with just one atom in bridging positions were silicon-bridged [1]FCPs [ER_x=SiPh₂, Sifc; fc stands for Fe(H₄C₅)₂] published by Osborne et al. [15]. 15 Years later, the first strained bis(benzene) complexes, SiPh₂-bridged [1]metalloarenophanes (C) with vanadium and chromium, were published by Elschenbroich et al. [16]. In 2004–2005, the research groups of Tamm, Elschenbroich, and Braunschweig, respectively, described the first heteroleptic metallocyclophanes of type D (M=Ti [17], V [18], Cr [19]).

It was Manners et al. who finally realized the use of [1]FCPs as monomers for ring-opening polymerization (ROP) and showed that sila[1]ferrocenophanes give poly(ferrocenylsilane)s (PFSs) with high molecular weights [*M*_w (R=Me)=5.2 × 10⁵ Da relative to PS; Scheme 1] [20]. This discovery kick-started tremendous research efforts and, to date, applying the well-established methods of thermal, transition-metal-catalyzed, photolytic, and anionic ROP for FCPs is an elegant way for the preparation of well-defined metallopolymers [21].

The most developed strained sandwich compounds are silicon-bridged [1]FCPs (A; Fig. 1), which can undergo living polymerizations [21–23] allowing for the preparation of block copolymers. PFS with SiMe₂-bridging moieties (R=Me; Scheme 1) is partially crystalline, causing block copolymers to form rod- or plate-shaped micelles in block-selective solvents with PFS as the core. These micelles are living and grow to larger micelles of uniform lengths through the addition of further unimers. This crystallization-driven self-assembly (CDSA) of amphiphilic block copolymers has been used recently as bottom-up approach for the fabrication of uniform nanomaterials (see [24–26] for selected recent publications). Compared to silicon-bridged [1]FCPs, other strained sandwich compounds are far less developed and only [1]FCPs bridged by germanium [27] and phosphorus [28–32], and [2]FCPs bridged by carbon [33] could be polymerized with control over molecular weights and molecular weight distributions.

¹ We define [*n*]metallocyclophanes similar as IUPAC defined cyclophanes by using the term mancude-ring systems [“rings having (formally) the maximum number of noncumulative double bonds”; IUPAC Gold book (<http://goldbook.iupac.org/>)]. Therefore, metal-containing “phanes” with metals sandwiched by mancude-ring systems will be referred to as metallocyclophanes. The subgroup where all π -coordinated ligands are cyclopentadienyl derivatives will be called metallocenophanes; the subgroup where they are benzene derivatives will be called metalloarenophanes.

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